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BARIUM-CONTAINING GLASS AS AN EFFICIENT SUBSTITUTE FOR HIGH-LEAD GLASS IN THE PRODUCTION OF LIGHT SOURCES

V. V. Lityushkin,[1] A. I. Kovalenko,[1] A. P. Sivko,[1] L. P. Smirnova,[1] and M. A. Filimonova[1]

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An analysis of known barium crystals and barium-containing electrovacuum glasses is provided. The possibility and expediency of their use in the production of lighting sources is demonstrated. The properties of new environmentally safe electrovacuum glass that can be produced using the known designs of glass-melting furnaces and molding methods are described.

High-lead glasses with PbO mass content equal to 20 and 30% are commonly used in the production of tubes for powerful incandescent lamps or gas-discharge light sources [1, 2]. Such glass is convenient in the assembly of vacuum electric equipment but is not environment-friendly in melting, since its batch contains red lead or lead monoxide, which are toxic components of the top-grade category, and up to 14% PbO evaporates from the glass mirror surface. Such glass is expensive to produce, primarily because of the use of expensive raw material for introducing PbO, and because of the need to pay environmental pollution penalties or to construct complicated sanitary and aspiration-environmental systems for the purification of waste gases resulting from lead dust and vapor lead compounds. The production of lead glasses has to be located far from residential quarters. Therefore, the time has come to abandon lead-containing glasses used in the light source production and replace them by lead-free glasses with similar physicochemical glasses. These conditions are best satisfied by glasses containing BaO and substantial quantities of alkaline oxides (OST 11.027.010–75) [3, 4].

Glasses known as barium crystal with BaO mass content up to 20% and total content of alkaline oxides up to 18% have recently gained wide acceptance. The TCLE of such glasses is $(99 - 109) \times 10^{-7}\,K^{-1}$ and they are soldered to platinite. They have low softening point and viscosity 10^{10} Pa · sec (510 – 520°C), rather high temperature $T_k - 100$ (290 – 300°C), and are easily melted, molded, and heat-treated. Similar properties are exhibited by other barium-containing electrovacuum glasses used in the production of black-and-white and color picture tubes, as well as some components (outer shell, stems, internal pieces) in the production of electric vacuum equipment (Table 1).

Thus, in the synthesis of new, more environmentally safe glasses for luminescent lamps and powerful incandescent lamps whose properties correlate with the properties of high-lead glasses, it is necessary to substitute BaO for PbO and introduce a third alkaline oxide, as well as halogens, in order to reduce the glass softening point. To increase the specific resistance (temperature $T_k - 100$), a small amount of alkaline-earth oxides should be introduced in the composition.

The Lisma JSC synthesized and successfully implemented a new glass composition free of PbO containing three alkaline oxides, in which $T_k - 100$ is over 300°C and the TCLE and specific resistance are close to the same parameters in glasses S93–1 and SL93–2 (see Table 1 and Fig. 1)

The lower glass softening temperature and the high heat resistance contribute to the formation of coordinated seals with the platinite group glasses. Due to the use of tubes with smaller thickness of glass, uniform distribution of the glass melt in the seal, and higher heat resistance of the new glass compared to S93–1 and SL93–2 glasses, the waste generated by cracking of articles at the stage of making stems and sealing lamps was decreased. The barium-containing glass contributes to the creation of an environment-friendly situation both in the glass-melting zone and in the zone of assembly of electrovacuum products and lighting sources.

The batch was mixed from top-quality materials. No adjustments were needed on the batch preparation line.

After crushing cullet to fragments sized 5 – 10 mm, it was loaded directly on the conveyor belt on the top of the batch and in this way the mixture arrived at the loading hopper of the furnace.

[1] Lisma Joint-Stock Company, Saransk, Russia.

TABLE 1

Parameter*	Barium crystals			Glass for picture tubes, electron-beam tubes and electrovaccum instruments					Synthesized glass composition for light sources
	1	2	3	713	S93-2	S93-5	S93-7	S97-1	
Mass content, %:									
BaO	17.0	20.0	20.0	12.0	12.0	11.0	12.0	16.2	12.0
alkaline oxides	17.5	18.8	18.0	14.4	14.4	16.0	14.6	15.5	15.0
halogens	-			0.8	0.8	0.9	0.6		0.3
TCLE within the temperature interval of 20 - 300°C, 10^{-7} K^{-1}	107.0	107.0	109.0	93.2	93.0	93.5	93.7	97.0	97.0
Softening point, °C:									
for viscosity 10^{10} Pa · sec	520	510	510	520	510	510	510	520	505
for viscosity $10^{6.6}$ Pa · sec (Littleton point)	620	620	620	625	620	620	620	625	625
Heat resistance, °C, at least	115	110	110	135	126	126	110	120	120
Temperature corresponding to volume resistivity 10^8 Ω · m (T_k – 100), °C, at least	290	300	300	290	280	280	280	300	320
Density, g/cm³	2.6	2.6	2.6	2.58	2.5	2.5	2.5	2.5	2.58

* The chemical resistance (weight loss with respect to water) of all samples was equal to 0.22%.

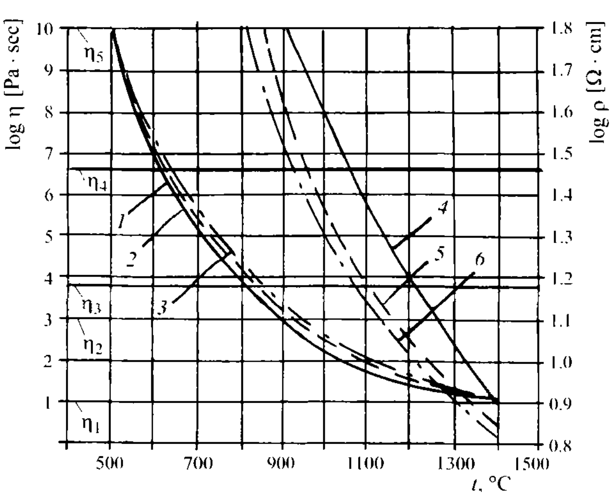

Fig. 1. Viscosity η and electric resistivity ρ versus temperature: *1*, *2*, and *3* are the viscosities of glasses S93-1, SL93-2, and the synthesized glass, respectively; *4*, *5*, and *6* are the volume resistivities of glasses S93-1, S93-2 and the synthesized glass, respectively; η_1) glass melt clarification, η_2) tube molding by the Wello method; η_3) tube molding by the Danner method, η_4) is the Littleton softening point; η_5) dilatometric deformation point.

Glass was melted in the glass-melting furnace described in [2].

A specific feature of barium-containing glasses consists in the fact that the cristobalite film, which in other cases transforms into crust and causes such flaws as cords and threads, is not formed either in the melting or the working zone.

The method does not require discharge of the glass melt or covering the glass melt surface by plates. However, the introduction of halogens into the composition degrades the crystallizing capacity of the glass and leads to the formation of crystallized sites inside sharp angles of the channels and the system of feeding the glass-melt band to the tube-molding nozzle using the Danner method. Crystals are entrained in the glass melt working flow and occasionally cause the formation of opaque or clear stones in tubes.

This drawback was eliminated by heating the working zone and channels, and special temperature conditions were selected for molding.

In order to produce tubes with a uniform distribution of glass melt along the tube circumference and length, the speed of glass drawing was increased. The disc configuration was modified, which made it possible to bring the stem molded from a disk as close as possible to the inner tube surface in sealing luminescent lamps.

After industrial tests, the Lisma JSC completely abandoned the use of lead-containing glasses and changed over to barium-containing glasses in the assembly of incandescent and luminescent lamps.

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